Interfacial Li-ion Localization in Hierarchical Carbon Anodes

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ABSTRACT: An understanding of the nanoscale structure and energetics of carbon composites is critical for their applications in electric energy storage. Here, we study the properties of carbon anodes synthesized from low-cost renewable lignin biopolymers for use in energy storage applications such as Li-ion batteries. The anodes possess both nanoscale and mesoscale order, consisting of carbon nanocrystallites distributed within an amorphous carbon matrix. Molecular dynamics simulations of an experimentally validated model of the anode is used to elucidate the nature of Li-ion storage. We report the discovery of a novel mechanism of Li-ion storage, one in which Li^+ is not intercalated between layers of carbon (as is the case in graphitic anodes), but rather is localized at the interface of crystalline carbon domains. In particular, the effects of Li-ion binding energy on the Li-Li, Li-H, and Li-C pair distribution functions are revealed, along with the effect on charge distribution. Lastly, the atomic environments surrounding the Li-ions

are grouped on the basis of ion energy and then convolved into archetypal structural motifs that reveal deep insight into the geometry of ion localization in disordered systems.

KEYWORDS: Li-ion batteries, anodes, carbon, composites, interface, capacity, charge

1. Introduction

Low-cost, high quality lithium-ion batteries are a desirable product in a market that is moving towards cleaner, less expensive, and more efficient energy [1]. The manufacturing of these batteries occurs with a trade-off between cost and effectiveness. Intercalation-based batteries (such as Li-ion batteries) require rapid transport of ions through the bulk active material and across the SEI into the electrolyte. Nanostructuring is an effective method for reducing diffusion lengths and enabling high rate performance and/or high capacity; however, the process of manufacturing unbound nanomaterials is difficult, and the methods involved incur a steep financial penalty [1]. On the other hand, batteries developed from low-cost materials are produced at a charge capacity, cycling capability, or safety penalty [1]. Recently however, materials derived from abundant, low-cost lignin sources show promise in achieving a good balance between cost and performance. The advanced carbon fiber technologies utilized at Oak Ridge National Laboratory (ORNL) to process lignin yield superior anode materials in the form of all-carbon composites composed of nanoscale crystalline domains dispersed within an amorphous matrix [2]. Carbon-carbon composite materials have many advantages including high reversible capacity, low irreversible capacity loss, high cycle life due to strong mechanical integrity, and enhanced safety because of a lack of substrate dissolution during overcharge [3].

Historically, most studies have sought to understand the nature of lithium storage in carbon anodes by focusing on homogeneous or non-hierarchical materials (e.g. graphite). For those materials, it has been experimentally determined that Li^+ intercalates between adjacent graphitic planes. More recent work has focused on utilizing nanomaterials as efficient anode materials [4]; however, these nanomaterials usually incur a steep manufacturing cost [1].

A significant amount of research was performed on carbon anode materials derived from biomass in the mid-1990s in order to elucidate the mechanism of Li-ion storage. Dahn et al. proposed three distinct mechanisms responsible for ion localization: 1) Li-ion intercalation occurs between layers of graphitic carbon, but not between layers that exhibits high turbostratic disorder 2) the maximum amount of lithium that can be inserted is proportional to the atomic ratio of hydrogen to carbon, suggesting that “lithium binds somehow in the vicinity of the H atoms” and 3) in materials that are predominantly composed of loose layers of graphene, lithium appears to adsorb onto both sides of the carbon sheets [5]. Zheng et al. find a “striking correlation” between the H/C ratio and Li-ion capacity and conjecture that the phenomenon is due to binding of Li in the vicinity of hydrogen atoms. They note that this high charge capacity comes with a penalty, as the anode voltage profiles exhibit a large hysteresis — i.e., the voltage delivered during anode discharge is significantly lower than that required for the charging process [6]. In a subsequent study, they show that lithium must overcome an energy barrier before it can localize near edge-terminating hydrogen atoms. They hypothesize that reducing this energy barrier is paramount to decreasing the hysteresis penalty.

Approaching the topic computationally, Papanek et al. perform static semiempirical calculations of planar hydrocarbons at the MNDO/AM1 level and reveal that the correlation between the H/C ratio and ion capacity is partially attributable to Li binding at H-terminated edges of hexagonal carbon fragments. They note that the local environment resembles that of $C_2H_2Li_2$ [7]. Röthlisberger and Klein find a similar $C_2H_2Li_2$ geometry in ab initio molecular dynamics simulations [8].

Herein, we report the discovery of a novel mechanism of Li-ion storage in hierarchical carbon composite anode materials—a mechanism in which Li^+ is not intercalated between layers of

carbon, but rather localized at the interface of crystalline carbon domains. We determine this by performing reactive molecular dynamics simulations on atomistic models of the experimental carbon anodes. We characterize Li-ion localization using pair distribution functions and three-dimensional density plots, and we also report how the localization changes as a function of ion energy. These findings imply that the charge capacity of these types of hierarchical materials is at least partially proportional to the surface area of the phase boundary.

2. Methods

Experimentally, the structure of the carbon composite varies as a function of the lignin pyrolysis temperature. Three properties in particular characterize the bulk of the variation: the density of the composite, the size of the nanocrystallites embedded within the composite, and the volume fraction of crystalline (vs amorphous) carbon. In a previous study of these materials [9], we developed a collection of atomistic models with different values for these three properties and used molecular dynamics (MD) simulations to understand the structure of the uncharged (unlithiated) anodes. For this work, we study one of the models in the collection — in particular, the model with properties that match the experimentally measured properties of the composite pyrolyzed at 1500 °C.[2] This composite has a density of 1.51 g/cm³, contains nanocrystallites 7 Å in radius, and is composed of equal parts crystalline and amorphous carbon by volume. The high number of atoms in the model (75,795 C, 32,353 H, and 5,012 Li) is necessary to correctly capture all of the experimentally observed nanoscale structural features, including the presence of phase boundaries.

For the previous study of the uncharged composite systems [9], the OPLS-AA forcefield [10] was chosen for the MD simulation in order to allow structural relaxation over a long period of

time. We found that the structural characteristics of the equilibrated model closely matched the features revealed experimentally via neutron scattering, thus validating our model and choice of potential [9].

For this work, a computational method that accurately accounts for the chemical reactivity of Li^+ was necessary. As it is not currently feasible to directly use quantum chemical techniques to study such large systems, we instead utilized ReaxFF, a reactive MD forcefield that addresses both the size and accuracy requirements of the simulation [11–13]. The specific ReaxFF potential used here was developed on the basis of quantum chemical calculations and is designed to account for chemical interactions between lithium, carbon, and hydrogen [14,15]. The design of the forcefield accounts for charge transfer between Li-ions and the surrounding environment by performing a charge equilibration calculation at each step of the MD simulation. This potential has been successfully used to understand the fracture mechanisms of lithiated graphene [16].

For the MD run, the uncharged computational model from the previous study was first re-equilibrated using ReaxFF in the canonical (NVT) ensemble with a Nosé-Hoover thermostat [17,18]. Li-ions were then added, and a minimization of the total system energy was performed using the conjugate gradient method until convergence to a local energy minimum was reached. The system was then equilibrated at 298 K for a duration of 224 ps and with a timestep of 0.25 fs. LAMMPS [19] was used to perform the simulation.

We investigated two concentrations of Li^+ : a high ion loading at 147.8 mAh g^{-1} , and a lower ion loading at 19.8 mAh g^{-1} . The high loading value was selected as the maximum charge capacity for this particular anode material [2] (with the assumption that each unit of positive electric charge [e^+] corresponds to exactly one Li^+), and the low loading value was selected as

the value that would intercalate one Li^+ between two planes of a crystallite, given that all crystallites are occupied.

In order to guide the initial placement of lithium ions in the system, we intercalated the ions between the layers of the carbon nanocrystallites. Raju et al. showed that when lithium atoms are placed outside of isolated stacks of carbon layers, the atoms tend to migrate into the spaces between the layers [14]. Because the redistribution processes of Li^+ may occur on timescales greater than that accessible to atomistic simulation, we investigated two initial conditions for each concentration of Li^+ : one in which all Li^+ are initially intercalated within planes of the graphitic nanoparticles, and another in which all ions are placed in the amorphous domain.

3. Results

A snapshot of the equilibrated system is shown in Figure 1. From the snapshot, it is immediately clear that Li-ions do not remain strictly localized within the carbon nanocrystallites. In order to determine the extent of Li-ion migration out of the carbon nanocrystallites, a smaller (yet compositionally identical) system containing just one nanocrystallite embedded within an amorphous carbon matrix was created and simulated for a duration of 2 ns. The results from this simulation (shown in Figure 2) highlight the egress of Li-ions from the interior vacancies of the nanocrystallite to the interfacial boundary separating the crystalline and amorphous carbon domains.

Within carbon anodes, an irreversible capacity loss occurs when Li-ions bind too strongly to the encompassing environment; the high adsorption energy leads to effectively infinite adsorbate stay times. Conversely, a failure to store charge occurs when Li-ions bind too loosely, resulting

in low charge capacity. In order to understand the mobility of the ions in the carbon composite, we study the localization of Li-ions as a function of their energy and the local environment.

Figure 1. The hierarchical carbon anode model after equilibration. Atoms are colored by type: amorphous carbon is blue, crystalline carbon is green, hydrogen atoms are white, and lithium ions are yellow. This simulation corresponds to a loading of 147.8 mAh g^{-1} and an initial condition in which all Li atoms were initially intercalated within the crystalline domain.

Figure 2. A small composite system with Li-ions intercalated in the crystalline domain (a) pre-equilibration and (b) post-equilibration. For clarity, the amorphous carbon matrix and hydrogen atoms surrounding the carbon nanocrystallite are rendered invisible.

The distribution of Li-ion energies is shown in Figure 3. This is the probability density function for finding a Li-ion at a specific potential energy within the simulation model. For equivalent levels of ion loading, the distributions of binding energies differ somewhat as a function of initial condition, indicating that true Li-ion equilibration occurs on a much longer time scale than MD simulation allows. However, the data does reveal several insights. First, conventionally, an adsorption energy of ~ 10 kcal/mol is considered the threshold between physisorption and chemisorption [20–22]. It is clear from Figure 3 that both chemisorption and physisorption occur within the hierarchical carbon anode. Second, a high charge density is necessary to push Li-ions into the realm of chemisorption. This can be stated in an alternative way. In physisorption, deep binding sites are occupied first and weak sites later, resulting in a binding energy that weakens with an increase in loading. Here, the opposite trend is observed. The average binding at high loading is stronger than at low loading because strong binding sites are created only with the additional loading of Li^+ . This suggests a cooperative aggregation of

Li^+ . Such a phenomenon can be confirmed through an examination of pair distributions functions.

Figure 3. Probability density function of the distribution of Li-ion binding energies in the equilibrated carbon anode for (a) high amorphous loading, (b) high crystalline loading, (c) low amorphous loading, and (d) low crystalline loading.

The pair distribution functions (PDFs) for Li-Li, Li-H, and Li-C pairs are shown in Figure 4 for a selection of Li-ion energy ranges, for a loading of 147.8 mAh g^{-1} , and for an initial condition in which all atoms were initially localized within the amorphous domain. For the Li-Li PDF (Figure 4a), the highest density peak occurs when Li-ions are strongly bound (chemisorbed). This trend reverses for the Li-C PDF (Figure 4c), as the highest peak occurs when Li-ions are weakly bound (physisorbed). The most interesting observation is in the Li-H PDF (Figure 4b), however, as the highest density peak occurs at a moderate energy level at the boundary of the chemisorption/physisorption transition ($\sim 12 \text{ kcal/mol}$). This suggests that specific types of Li-H pairs exist for particular Li-ion energies. Furthermore, because the Li-H peaks are much

narrower than the Li-Li and Li-C peaks, this implies that the distances between Li-H atom pairs fall within a tight range.

Figure 4. PDFs for (a) Li-Li, (b) Li-H, and (c) Li-C pairs of atoms.

In order to gain a deeper insight into the nature of Li-ion localization, it is important to understand not just the radial component of the environment surrounding a given ion, but the angular components as well. To this end, a novel technique has been developed to extract 3D structural motifs from atomic position data. The local atomic environments surrounding each Li-ion are sorted into one of three groups on the basis of the ion’s binding energy. We then note that the central atom’s energy is invariant to certain transformations of its local environment. These transformations include rotations, inversions, and permutations of atoms of the same type. In order to isolate the symmetry-invariant information contained within the environment, the atomic configurations within each group are rotated and reflected in such a way as to globally maximize their overlap. The results of this process are shown in Figure 5.

Figure 5. 3D density distributions of Li (green) and H (white) for (a) strong Li-ion binding energies, (b) moderate Li-ion binding energies, and (c) weak Li-ion binding energies. Each distribution is centered about a Li-ion, which is not shown.

In Figure 5, we present three-dimensional density distributions of atoms around a central Li atom for: (a) strong binding energies (-20.86 to -14.04 kcal/mol), (b) moderate binding energies (-11.04 to -10.71 kcal/mol), and (c) weak binding energies (-8.20 to -1.08 kcal/mol). It is apparent from Figure 5(a) that the most structured environment is the one surrounding the most

strongly bound Li-ions. The neighboring hydrogen atoms are localized into tight regions of space, and the neighboring Li-ions are located shortly beyond the hydrogens. The Li-ions are arranged at the corners of a cube. The H atoms are arranged at the faces of a cube. Note that a stoichiometry of a Li-H complex cannot be directly extracted from these images since the density contours of the two species are different. (One can think of the white clouds corresponding to H as having a lower occupancy than the green clouds describing the Li^+ distribution). This cube represents an archetypal structure averaged over all strongly bound Li^+ . No single local environment observed in the simulation corresponds to this reference. On the contrary, manifestations in the simulation can be considered highly defective perturbations of this structure. The defects are due to (1) the disordered nature of the carbon composite and (2) thermal energy.

From Figures 5(b) and 5(c) it is seen that as the Li-ions become more weakly bound, two changes occur. First, the clouds expand in size, corresponding to the local environment becoming more disordered. Second, the neighboring Li-ions are found at a greater distance from the central ion. This further validates the idea that strong binding is a result of a cooperative Li and H effect.

Lastly, we look at the relationship between charge and binding energy. Figure S.4 in the supplementary information reveals a tight correlation between the two properties. Chemisorbed Li-ions tend to share their charge with neighboring atoms, whereas physisorbed ions tend to retain more of their +1 ionization. Interestingly, in this composite material, the average charge of Li^+ in the anode is found to be $0.28 e^+$, indicating a state of partial charge transfer between the atom and the formal Li^{+1} ion.

In Figure 6, the carbon-carbon PDF from the simulation at the high ion concentration with initial positions in the amorphous domain is compared to experimental neutron scattering data

for a lignin carbon composite [2,9] in both the uncharged and lithiated states. From this plot, it is evident that the experimental PDF for the lignin-based anode closely resembles the PDF of our computational model. The change upon lithiation in the carbon composite material is negligible, an indication of the lack of atomic level restructuring of the anode during the charging process, resulting in the high cyclability of these materials. This lack of restructuring also contrasts with the restructuring that occurs in graphite during the charging process [23]. The X-ray diffraction peak for Li-intercalated graphite reveals a significant change in the interlayer spacing between planes of carbon. This provides experimental evidence for a mechanism of ion storage in our materials that differs from that of conventional graphitic anodes.

Figure 6. Comparison of the carbon (C-C) PDFs for (a) the uncharged materials and (b) the lithiated materials. The PDF of the computational model system was calculated using atom positions from the MD simulation results, and the PDF for the lignin-derived anode was obtained experimentally via neutron diffraction using the NOMAD beam line at the Spallation Neutron Source at Oak Ridge National Laboratory.

4. Conclusion

By inspecting the data in a variety of ways, a clear trend emerges for the nature of Li-ion localization in these hierarchical carbon materials. Most notably — and counter to the nature of ion storage in graphitic carbons — Li-ions do not intercalate between the layers of $r = 7 \text{ \AA}$ carbon nanocrystallites. The most energetically favorable positions for Li-ion storage are near the hydrogen atoms located at the interface between the crystalline and amorphous domains of carbon. Because hydrogen content scales with interface size, Li-ion storage capacity (and thus charge capacity) is proportional to the surface area of the interfacial boundary.

The binding energies of lithium are highly variable, ranging from chemisorption to physisorption. This heterogeneity in binding energy is partially captured in the PDFs, which show Li^+ aggregation for strongly bound Li^+ . For these composites, we have identified an archetypal structure of Li and H. Observed deviations from this structure reflect structural and thermal disorder.

For future work, it would be illuminating to determine the specific nanocrystallite size at which ion storage transitions from the surface to the interior.

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Author Contributions

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